



University of Groningen

Valorization of bio-based alcohols using catalytic technology

Kumalaputri, Angela Justina

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version Publisher's PDF, also known as Version of record

Publication date: 2017

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA): Kumalaputri, A. J. (2017). Valorization of bio-based alcohols using catalytic technology. University of Groningen.

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: https://www.rug.nl/library/open-access/self-archiving-pure/taverneamendment.

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Valorization of Bio-based Alcohols using Catalytic Technology

Angela Justina Kumalaputri

Paranymphs:

Dr. Idoia Hita Dr. Sanne W. L. Palstra

The research reported in thesis was partly supported by the EDGAR research program (Energy Delta Gas Research), as a part of the AGATE (Advanced Green Gas Technology) project. The Indonesian Directorate General of Higher Education (DIKTI) is acknowledged for providing a scholarship to AJK.

Cover design: Layout & Printing:

ISBN (printed version): 978-94-034-0140-9 ISBN (digital version): 978-94-034-0139-3

Angela Justina Kumalaputri & Stephen Surya D Lovebird design www.lovebird-design.com 978-94-034-0140-9 978-94-034-0139-3



Valorization of Bio-based Alcohols using Catalytic Technology

PhD thesis

to obtain the degree of PhD at the University of Groningen on the authority of the Rector Magnificus Prof. E. Sterken and in accordance with the decision by the College of Deans.

This thesis will be defended in public on

Friday 22 December 2017 at 14.30 hours

by

Angela Justina Kumalaputri

born on 06 February 1985 in Cirebon, Indonesië

Supervisors

Prof. H. J. Heeres Prof. K. Barta

Co-supervisor

Dr. P. J. Deuss

Assessment Committee

Prof. A. A. Broekhuis Prof. F. Picchioni Prof. K. Seshan

dedicated to Papi (†) & Mami (†)

Contents

Chapter 1		Introduction	11
	1.1 Backgro	und – Biomass-based vs fossil resources	13
	1.1.1	Biomass for chemicals	14
	1.2 Bio-bas	ed platform chemicals	15
	1.3 Selected	d platform chemicals for study in this thesis	17
	1.3.1	5-Hydroxymethylfurfural (HMF)	17
	1.3.2	2,5-Furandimethanol (FDM)	19
	1.3.3	2,5-Dimethylfuran (DMF)	21
	1.3.4	1,2,4-Benzenetriol (BTO)	22
	1.3.5	Glycerol	23
	1.3.6	Glycerol conversion to methane (green gas)	24
	1.4 Thesis o	putline	25
	References	1	28
Ch	apter 2	$Tunable \ and \ selective \ conversion \ of \ 5-HMF \ to \ 2,5-fur and imethanol$	
		and 2,5-dimethylfuran over copper-doped porous metal oxides	35
	2.1 Introdu	ction	37
	2.2 Results	and discussion	38
	2.2.1	Catalyst preparation and characterization	38
	2.2.2	Tunable and selective conversion of HMF to FDM or DMF	40
	2.2.3	Reaction pathways and intermediates	47
	2.2.4	Recyclability tests	54
	2.2.5	TEM measurements	55
	2.3 Conclus	sions	57
	2.4 Experimental section		58
	2.4.1	Catalyst preparation	58
	2.4.2	Catalyst test	59
	2.4.3	Catalyst recycling tests	59
	2.4.4	Continuous-flow experiment for FDM production	60
	Acknowled	gements	60
	References	;	60
	Supporting	Information	65
Ch	apter 3	Copper-zinc alloy nanopowder: a robust precious-metal-free cata-	
		lyst for the conversion of 5-hydroxymethylfurfural	77
	3.1 Introdu	ction	79
3.2 Results and discussion		and discussion	80
	3.3 Experir	nental section	87
3.4 Conclusions			88
	Acknowledgements		
References			88
	Supporting	Information	93

Chapter 4		Lewis acid catalysed conversion of 5-hydroxymethylfurfural to			
		1,2,4 benzenetriol, an overlooked bio-based compound	113		
4.1 In	troduc	ction	115		
4.2 Re	sults	and discussion	116		
4.	.2.1	Exploratory reactions including 5,5'-BTO dimer formation	116		
4.	.2.2	Lewis acid catalysed formation of BTO at subcritical conditions	118		
4.	.2.3	Further optimization of the reaction conditions	121		
4.	.2.4	Catalytic hydrodeoxygenation of BTO	123		
4.3 Co	onclus	ions	124		
Ackno	owledg	gements	125		
Refer	ences		126		
Supp	orting	Information	129		
Chapter	Chapter 5 Glycerol methanation in supercritical water: a systematic catalyst				
		screening study using mono- and bimetallic supported Ru	and Ni		
		catalysts	147		
5.1 In	troduc	tion	149		
5.2 M	5.2 Materials and methods		151		
5.3 Ex	5.3 Experimental procedure		152		
5.	.3.1	Catalyst preparation	152		
5.	.3.2	Description of the batch set-up	152		
5.	.3.3	Analysis	153		
5.	.3.4	Catalyst characterization	154		
5.4 Re	5.4 Results and discussion		156		
5.	.4.1	Blank experiments	156		
5.	.4.2	Catalyst screening using the monometallic catalysts	156		
5.	.4.3	Catalyst screening using bimetallic Ni-Ru catalysts	159		
5.	.4.4	Catalyst selection for dedicated experiments	161		
5.	.4.5	Optimization of catalyst intake and catalyst metal loading	161		
5.	.4.6	Catalyst stability	162		
5.	.4.7	Catalyst characterization	164		
5.5 Co	onclus	ions	167		
Acknowledgements References		gements	168		
			168		
Supp	172				
Summary					
Samenvatting					
Acknow	Acknowledgements				
List of Publications					